

(12) UK Patent Application (19) GB (11) 2 370 646 (13) A

(43) Date of A Publication 03.07.2002

(21) Application No 0124648.7

(22) Date of Filing 15.10.2001

(30) Priority Data

(31) 10053979

(32) 31.10.2000

(33) DE

(71) Applicant(s)

Carl-Zeiss-Stiftung
(Incorporated in the Federal Republic of Germany)
Schott Glas, Hattenbergstrasse 10, 55122 Mainz,
Federal Republic of Germany

(72) Inventor(s)

Gunter Tauber

(74) Agent and/or Address for Service

Marks & Clerk
Alpha Tower, Suffolk Street Queensway,
BIRMINGHAM, B1 1TT, United Kingdom

(51) INT CL⁷

G01N 27/30 // G01N 27/403

(52) UK CL (Edition T)

**G1N NBEX NBPX N25B N25C3H1 N25C3H2 N25C4B2
N25C4E**

(56) Documents Cited

DE 003702501 A

US 4333812 A

US 4012308 A

(58) Field of Search

**UK CL (Edition T) G1N NBEG NBEM NBEX NBKX
NBPX**

INT CL⁷ G01N 27/28 27/30 27/36 27/403

Online: EPODOC, JAPIO, WPI

(54) Abstract Title

Electrochemical measuring device

(57) The present invention describes an electrochemical measuring device with a measuring electrode and a reference electrode (6) in a closed tubular casing (1) of glass comprising an inner chamber (2) with an inner branching electrode (3) for the measuring electrode and a glass pH membrane (4), an annular outer chamber (5) arranged concentrically for receiving the reference electrolyte (6) with the branching electrode (3) and a diaphragm (8) arranged in the lower portion of the tubular casing (1), wherein the annular outer chamber (5) is completely filled with at least one reference electrolyte (6) and a resilient body (9) is arranged in the annular outer chamber.

FIG 1

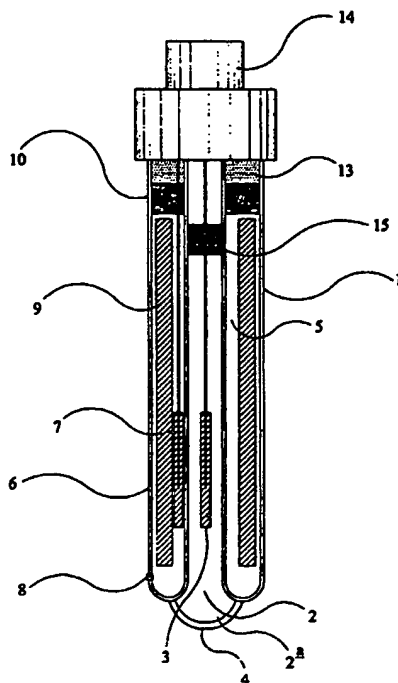


FIG 1

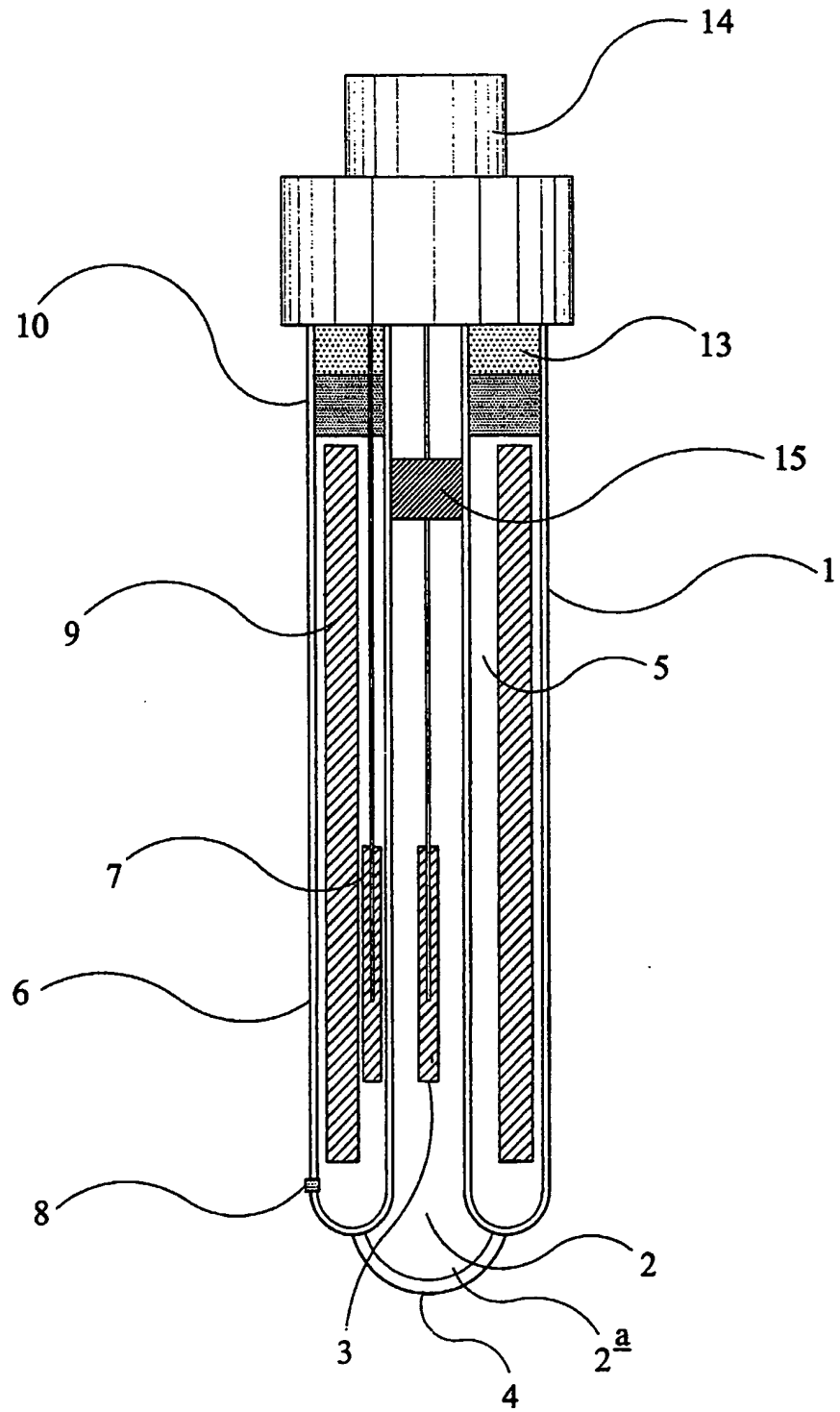
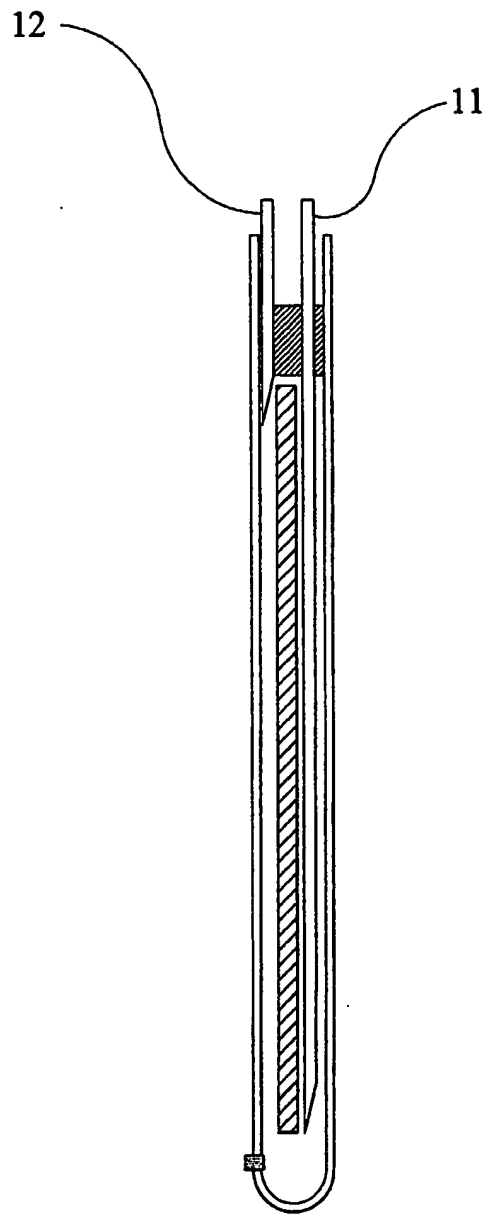


FIG 2



Electrochemical Measuring Device

The present invention relates to an electrochemical measuring device method for its production.

In order to monitor chemical and biological processes, electrochemical cells are used for measuring ion activities, in particular H-ion activities. The electrochemical cells comprise a measuring electrode and a reference electrode. The measuring and reference electrodes can be formed separately or can be present in one body in the form of a single-rod measuring device. An essential pre-condition for a reliable monitoring of the process is that the reference electrode should deliver a stable and reproducible electrical voltage. The reference electrode can be an electrochemical half element or half cell.

Reference electrodes generally comprise a branched element in the form of an electrode of the second type which dips into a reference electrolyte. The reference electrolyte is usually a concentrated potassium chloride solution. In this case the reference electrolyte is present in a container which is formed by a casing of electrically non-conductive material, such as glass or plastics material.

The electrolytic contact between the branched element of the reference electrode and the measuring medium is made by a diaphragm arranged in the casing wall. The diaphragm is frequently a porous ceramic pin. The measuring medium is a solution or suspension in water of the measurement substance to be investigated. The measuring medium can contaminate the diaphragm or can penetrate into the reference electrolyte and dilute it. In both cases, an uncontrollable change in voltage and thus a falsification of the

measurement values can occur. This is the case in particular when the measurements extend over a prolonged period of time or are frequently repeated.

In order to prevent the penetration of measuring medium through the diaphragm and into the reference electrolyte, pressure sensing devices are frequently used. As a result, a pressure – which is higher than that of the measuring medium – is maintained in the reference electrolyte. In this case, the procedure is generally carried out at an overpressure of from 0.2 to 0.5 bar. This can be achieved by fitting the measuring device in a pressure chamber and arranging for it to be acted upon by compressed air. Since strict demands are made upon the degree of sterility as a rule, measuring devices have to withstand the conditions of steam sterilization at temperatures of up to 135°C and pressures of up to 3.5 bar.

Measuring devices of this type require a certain amount of maintenance, such as topping up with reference electrolyte, acting upon with pressure and greasing of seals, such as O-rings. In the case of incorrect or omitted maintenance, defective measurements can occur, since the stability of the reference electrode is no longer provided. In order to avoid these drawbacks, measuring devices have been developed in which the reference electrolyte, such as a 3-molar or saturated potassium chloride solution, is present in the form of a gel or is thickened with a thickening agent, such as highly dispersed silicic acid.

In the case of reference electrodes or measuring devices a gas cushion, which allows the thermal expansion of the gel-like or thickened electrolyte, always has to be present in the space of the reference electrode. The penetration of

measuring medium through the diaphragm can be prevented in the reference electrodes or measuring devices if a pressure equalization is provided between the measuring medium and the reference electrolyte. In this case, the filling opening has a disadvantageous effect since a turbulent flow, which can be associated with the formation of foam, is generally present in the reactors. The measuring medium in the form of squirts or foam passes through the filling opening and into the space of the reference electrode and results in a change in the same way as the penetration through the diaphragm. The dilution of the reference electrolyte has an adverse effect upon the accuracy of measurement.

A pH measuring device is known from DE-A-37 02 501 for monitoring microbiological processes with a measuring electrode and a reference electrode in a closed tubular casing of glass. The tubular casing comprises an inner chamber with a branched system for the measuring electrode and with an ion-selective membrane and an annular outer chamber arranged concentrically for receiving a gel-like reference electrolyte and a branched system for the reference electrode. The reference electrolyte can be brought into contact with a measuring medium by way of a diaphragm arranged in the lower portion of the tubular casing dipping into the measuring medium present in a bio-reactor. A cavity, in which a gas under pressure and connected to the reference electrolyte is present, is provided in the pH measuring device above the reference electrolyte in the annular chamber in the portion of the tubular casing. An internal pressure which is greater than that of the measuring medium can be maintained by the gas in the chamber of the tubular casing. A supply means – which is fastened in a gas-tight manner in the wall of the casing and which can be closed – for the gas opens into the cavity. In the upper portion of the casing, a cavity for receiving a gas under pressure, such as compressed air, is present in an annular chamber. A supply means for the gas

opens into the cavity. The supply means is a platinum capillary with an external diameter of from 0.3 to 0.5 mm. This platinum capillary is fastened in a gas-tight manner in the wall of the casing at the melting point by melting-in. After the gas under pressure has been supplied, the platinum capillary acting as the supply means can be closed in a gas-tight manner by being squeezed off by pliers at the squeezing point. In the annular chamber, a cushion of foamed material, which covers the reference electrolyte and abuts against the walls of the chamber, is present between the reference electrolyte and the cavity. As a result, the reference electrolyte can be prevented from flowing out during the transportation of the pH measuring device.

For stressing with pressure the reference electrode has a platinum capillary which is melted into the tubular casing. By dissolving in the gel, the air can diffuse through the diaphragm and give way, as a result of which the internal pressure drops. This results in a limited storage life of the electrode. In the event of mechanical damage to the glass shaft the electrode can shatter in the manner of an explosion. As the temperature rises, the pressure in the glass container also increases, as a result of which there is a greater risk of injury.

The object of the present invention is to provide a stable and reliable novel electrochemical measuring device and an economical and environmentally harmless method of producing an electrochemical measuring device, in which the risk of injury is avoided as far as possible.

The object of the present invention is attained by an electrochemical measuring device with a measuring electrode and a reference electrode in a closed tubular casing of glass comprising an inner chamber with an inner branching electrode for the measuring electrode and a pH glass membrane, an annular outer

chamber arranged concentrically for receiving a reference electrolyte with a branching electrode for the reference electrode and a diaphragm arranged in the lower portion of the tubular casing, wherein the annular outer chamber is adapted to be completely filled with at least one reference electrolyte, and at least one resilient body is arranged in the annular outer chamber.

In the electrochemical measuring device according to the invention, a resilient body is advantageously used to urge the delivered KCl electrolyte out of the diaphragm. The stressed springing body is probably present in the gel. The electrochemical measuring device advantageously has no compressed air in the inner space. In the event of damage to the glass body, the resilient body is slowly relieved of stressing and the gel is joined to the pieces of broken glass. Glass splinters flying around in the manner of an explosion is prevented. The electrochemical measuring device has a relatively long storage life, since no air which can diffuse through the diaphragm by dissolving in the gel is present in the inner space. The measuring device according to the invention is not susceptible to increases in temperature. A further advantage of the electrochemical measuring device according to the invention is that no platinum capillaries are used during the manufacture.

When the chamber is filled with the reference electrolyte under pressure, the resilient body is compressed. As it expands, the resiliently springing body exerts a force upon the gel. As a result of the expansion of the compressed resilient body, the gel flows at a defined speed out of the diaphragm and into the measuring solution, thereby ensuring a high degree of accuracy of measurement and a long service life of the measuring device.

A preferred embodiment of the invention is an electrochemical measuring

device where the resilient body is a metal spring with a piston or a polymer foam. It has been found that a metallic body in the form of a spring and a piston can be used as a resilient body with good results. Resilient bodies which essentially consist of a polymer foam likewise display very good results. The polymer foam contains air. The volume of the polymer foamed body preferably amounts to from 10% by vol. to 90% by vol., more preferably from 60% by vol. to 80% by vol., and particularly preferably from 65% by vol. to 75% by vol. of the volume of the annular outer chamber. The polymers used are preferably silicone, polyurethane or neoprenes for producing the polymer foam. All the variants according to the invention are highly suitable for increasing the pressure in the outer chamber in accordance with the requirements and thereby for ensuring that the electrolyte flows out of the diaphragm.

A preferred embodiment of the invention is an electrochemical measuring device where the resilient body occupies from 10% by vol. to 90% by vol., and preferably from 30% by vol. to 60% by vol. of the volume of the annular outer chamber. In this volume range for the resilient body very good results are achieved in the electrochemical measuring device. A constant pressure is produced over a prolonged period, and a reliable and trouble-free outflow of the reference electrolyte through the diaphragm is provided.

A preferred embodiment of the invention is an electrochemical measuring device where the pressure in the annular outer chamber amounts to from 0.5 bar to 4 bar. In this pressure range very good results are obtained with respect to the constant outflow of the reference electrolyte through the diaphragm.

A preferred embodiment of the invention is an electrochemical measuring

device where the reference electrolyte contains a heat-resistant thickening agent which is preferably produced on the basis of polyaryl amide or methyl cellulose.

According to the invention a method of producing an electrochemical measuring device is provided, in which the annular outer chamber arranged concentrically has

- a) at least one resilient body introduced into it,
- b) the reference electrode inserted into it,
- c) the annular outer chamber is closed with a seal,
- d) an aerating cannula passes through the seal,
- e) the annular outer chamber is completely filled with at least one reference electrolyte through at least one further cannula passing through the seal,
- f) the aerating cannula passes out of the seal,
- g) at least one reference electrolyte is introduced into the annular outer chamber until the pressure to be set is achieved, and
- h) the tubular casing is closed with a cast compound and the measuring device is provided with an attachment head.

The method according to the invention has the crucial advantage over the conventional methods that no compressed air is used when the measuring device is filled. The method according to the invention is significantly simpler and more inexpensive than the methods known in the prior art for producing an electrochemical measuring device.

The electrochemical measuring device according to the invention can be used to measure pH values, redox potentials or ion activities.

An embodiment of the present invention will now be described in greater detail with reference to the accompanying drawings, in which:

Fig. 1 is a schematic view of an electrochemical measuring device according to the present invention; and

Fig. 2 is a schematic cut-away view of part of the device of Fig. 1.

Referring now to Fig. 1, the electrochemical measuring device comprises a closed formed tubular casing (1) of glass and comprising an inner chamber (2) surrounded by an outer annular chamber (5) arranged concentrically.

The inner chamber (2) is closed in an upper region by a seal (15). In its lower region projecting beyond the annular chamber (5), the inner chamber (2) has a glass pH membrane (4) of ion-selective glass. The inner chamber (2) forms the actual measuring electrode and is provided with an inner branching electrode (3) for the measuring electrode. The branching electrode (3) is connected to a line – passing through the seal (15) to the outside – in an attachment head (14) with an electrical attachment. A rubber seal (10) and a cast compound (13) are provided in the top of the annular chamber (5) below the attachment head (14).

The annular chamber (5) forms the actual reference electrode comprising a gel-like reference electrolyte (6) and a branching electrode (7) for the reference electrode. The branching electrode (7) is connected to a line leading to the outside. A diaphragm (8), as a rule a porous ceramic pin, is present in the lower portion of the annular chamber (5). The reference electrolyte (6) present

in the chamber (5) can be brought into contact, by way of the diaphragm (8), with a measuring medium into which the measuring device dips at least in part.

A 3- to 4-molar potassium chloride solution with a thickening agent, such as for example an acrylamide compound, is used as the reference electrolyte (6). The reference electrolyte (6) has a viscosity of at least 10 pascal seconds. Instead of the acrylamide compound, other thickening agents such as methacrylamide, silicic acid, hydroxylated celluloses, methyl cellulose and polysaccharides can also be used. When selecting the thickening agent, it is only necessary to make sure that they are compatible with the salt of the electrolyte solution and can withstand temperatures of up to 135°C.

Disposed within the annular chamber (5) is an annular, resiliently compressible body (9) which, when compressed, serves to apply pressure to the electrolyte (6) to urge it through the diaphragm (8). Since a throughflow – which is small but not non-existent – of the gel-like reference electrolyte (6) through the diaphragm (8) and into the measuring medium constantly takes place, a ceramic pin with an average pore size of approximately 1 μm is used as the diaphragm (8). The dependency of the throughflow quantity of the reference electrolyte (6) upon its viscosity and the geometric parameters of the diaphragm (8) are used as parameters for selecting the diaphragm. In this case, it is specified that the throughflow of the gel-like reference electrolyte (6) through the diaphragm (8) amounts to 0.2 ml *per* month at an overpressure of approximately 1 bar in the chamber (5). In this way, it is possible in an individual case to determine by calculation the parameters of the measuring device, such as the dimensions of the casing (1), the viscosity of the reference electrolyte (6), the porosity of the diaphragm (8) and the ratio of the volumes of the reference electrolyte (6) to the resilient body (9), and to adjust them to the

respective purpose of application. It has been found that, even after repeated heating, the electrochemical measuring device has an internal pressure in the chamber (5) of at least 0.5 bar. As a result, the penetration of measuring medium into the reference electrolyte (6), and thus its changing the concentration, are prevented completely. This is shown in particular by stable and reproducible voltage values.

Referring now to Fig. 2, one cut-away portion of the chamber (5) is shown with an aerating capillary (11) and a filling capillary (12). This design is used for filling the chamber (5). The two capillaries are removed after the chamber (5) has been filled. The two capillaries are advantageously steel capillaries and not expensive platinum capillaries.

The electrochemical measuring device according to the invention is characterized by a high degree of stability of the measurement values. In addition, the electrochemical measuring device according to the invention is very reliable and displays constant and reproducible results in the case of repetition. It has no internal gas pressure and does not pose the risk of an explosion when used. The manufacture of the electrochemical measuring device according to the present invention is therefore economical since the expensive platinum cannula otherwise customary is not used.

Claims:

1. An electrochemical measuring device with a measuring electrode and a reference electrode in a closed tubular casing of glass comprising an inner chamber with an inner branching electrode for the measuring electrode and a glass pH membrane, an annular outer chamber arranged concentrically for receiving a reference electrolyte with a branching electrode for the reference electrode and diaphragm arranged in a lower portion of the tubular casing, wherein the annular outer chamber is completely filled with at least one reference electrolyte, and at least one resilient body is arranged in the annular outer chamber.
2. An electrochemical measuring device according to Claim 1, wherein the resilient body is a metal spring with a piston or a polymer foam.
3. An electrochemical measuring device according to Claim 1 or 2, wherein the resilient body occupies from 10% by vol. to 90% by vol. of the volume of the annular outer chamber.
4. An electrochemical measuring device according to Claim 3, wherein the resilient body occupies from 30% by vol. to 60% by vol. of the volume of the annular outer chamber.
5. An electrochemical measuring device according to any one of Claims 1 to 4, wherein the pressure in the annular outer chamber amounts to from 0.5 bar to 4 bar.
6. An electrochemical measuring device according to any one of Claims 1 to

5, wherein the reference electrolyte contains a heat-resistant thickening agent.

7. An electrochemical measuring device according to Claim 6, wherein the heat-resistant thickening agent is a polyaryl amide- or methyl cellulose-based thickening agent.
8. A method of producing an electrochemical measuring device according to any one of Claims 1 to 7, including the steps of
 - a) introducing said at least one resilient body and said reference electrode into said outer annular chamber,
 - b) closing the annular outer chamber with a seal,
 - c) passing an aerating cannula through the seal, and
 - d) completely filling the annular outer chamber with said at least one reference electrolyte through at least one further cannula passing through the seal,wherein
 - e) the aerating cannula passes out of the seal,
 - f) at least one reference electrolyte is introduced into the annular outer chamber until the pressure to be set is achieved, and
 - g) the tubular casing is closed with a cast compound and the measuring device is provided with an attachment head.

9. Use of an electrochemical measuring device according to one or more of Claims 1 to 7 for measuring pH values, redox potentials or ion activities.



INVESTOR IN PEOPLE

Application No: GB 0124648.7
Claims searched: 1-9

Examiner: Peter Mason
Date of search: 25 April 2002

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.T): G1N(B): NBPX, NBEG, NBEM, NBEX, NBKX

Int Cl (Ed.7): G01N: 27/28, 27/30, 27/36, 27/403

Other: Online: EPODOC, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	US 4,333,812 (BUKAMIER & RUPERT) See column 2, lines 24 - 52, and note spring arrangement 96 in figure 4.	1,2,5,6,7,9
X	US 4,012,308 (BECKMAN INSTRUMENTS INC) See column 2, lines 1 - 18 and note plug 20 in figure 1.	1,5,6,7,9
A	DE 37 02 501 A (DR W INGOLD) See whole document	-

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.